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SCIENCE FOR GLASS PRODUCTION

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$BaO–La_2O_3–B_2O_3–TiO_2–SiO_2$ GLASS PRODUCTION

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Partial sections of the system $BaO–La_2O_3–B_2O_3–TiO_2–SiO_2$ were studied and the regions of glassy-state stability are determined. The regular effects of titanium, lanthanum, and barium oxides on the crystallizability of the experimental glasses and on the optical and thermal properties were established. An optical glass with refractive index 1.81, average dispersion 0.0187, and CLTE $76.8 \times 10^{-7} K^{-1}$ was obtained. This glass can be recommended for high refractive-index optical lenses as well as for the light-guiding core in optical fibers.

Key words: rigid optical fiber, heat treatment, phase separation, refractive index, viscosity, lanthanum oxide, liquation.

The system $BaO–La_2O_3–B_2O_3–TiO_2–SiO_2$ is of interest from the standpoint of obtaining high refractive-index optical glass. Such glasses are finding applications in the production of rigid optical fiber and geometric-optics parts.

Optical glasses must satisfy a number of technological requirements. Specifically, they must be stable against phase separation, first and foremost, crystallization. This requirement is especially important for optical fibers drawn at temperatures 800 – 1000°C. Soaking at about 700°C is used to obtain fiber-optic articles from multifilament fiber.

It is well known that lanthanum oxide is used in superheavy crown and flint glasses [1]. The refractive index can be increased considerably by introducing lanthanum and titanium oxides, but their active influence on the phase separation process limits their content in glass.

The problem of the present research is to develop compositions for high refractive-index (of the order of 1.81) optical glass. The base system for developing optical glass is the system $La_2O_3–B_2O_3–SiO_2$ with component content from 20 to 60%.[3] Experiment planning with Scheffe's simplex-lattice designs was used to select the glass compositions [2].

Low-silica compositions are chosen because the glass-making temperature must not exceed 1400°C. This requirement is imposed because glass in which the mass content of coloring impurities must not exceed 10^{-7}% is made using platinum crucibles which remain undeformed to temperatures 1420°C.

A calculation of the refractive index by L. I. Demkina's method [3] for the chosen composition range of the system $La_2O_3–B_2O_3–SiO_2$ showed a large increase of this index with increasing La_2O_3 content. Substituting La_2O_3 for SiO_2 and B_2O_3 in amounts ranging from 20 to 60% makes it possible to increase the refractive index from 1.62 – 1.67 to 1.86.

Figure 1 shows the evaluated technological properties of $La_2O_3–B_2O_3–SiO_2$ glass synthesized at temperature 1400 ± 10°C.

The glass forming capacity of mixtures decreases with increasing lanthanum oxide content, so that mixtures with 40 – 60% La_2O_3 do not form a uniform melt and are highly prone to crystallization during production. Increasing the SiO_2 content to 50 – 60% promotes the formation of a silica skin on the melt surface. Melts with 40 – 60% B_2O_3 and 20 – 40% SiO_2 are characterized by the presence of stable liquation. Cooling melts separate into two glassy layers: transparent and opacified. This suggests that a region of stable liquation is present in high-boron low-silica compositions of the experimental system $La_2O_3–B_2O_3–SiO_2$.

X-ray phase analysis performed with a D8 Advance diffractometer (Bruker Company, Germany) shows that B_3LaO_6 and $LaBO_3$ precipitate as crystalline phases in the opacified layer.

The results of a Fourier spectroscopic study of liquating samples are displayed in Fig. 2. A considerable difference in

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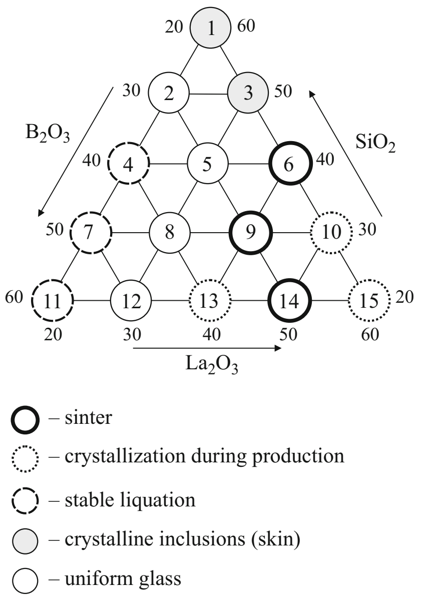

Fig. 1. Technological properties of La_2O_3–B_2O_3–SiO_2 glass: 1 – 15) numbers of the experimental glasses.

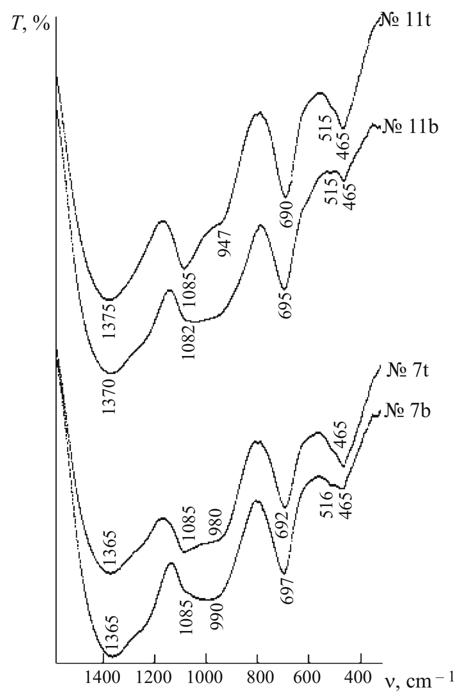

Fig. 2. IR spectra of liquating samples: 7t, 7b, 11t, 11b) numbers of the compositions of liquating samples with an indication of the layer [t) top; b) bottom].

the structure of liquating layers manifests as a change in the intensity of the absorption bands corresponding to the vibrations of the atoms in Si – O – Si bonds: stretching vibrations in the range 1000 – 900 cm^{-1} and deformation vibrations in the range 500 – 450 cm^{-1}. The stronger absorption in these spectral ranges indicates that SiO_2 predominates in the top layer of the glassy sample.

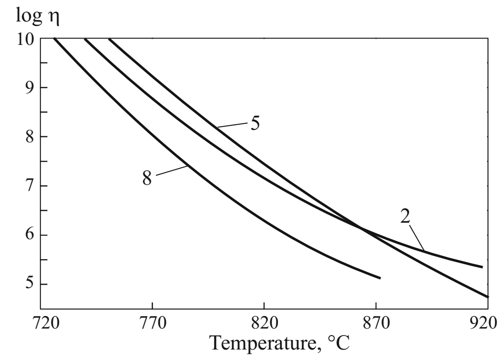

Fig. 3. Viscosity of La_2O_3–B_2O_3–SiO_2 experimental glass: 2, 5, and 8 are the compositions numbers of the experimental glasses.

The [BO_3] groups predominate in the bottom layer. This is indicated by the strong absorption band in the range 1300 – 1500 cm^{-1} peaking at 1365 – 1375 cm^{-1}. It can be asserted with some certainty that [BO_4] groups are also present in the structure of the samples; this is indicated by the absorption peaking at 1085 cm^{-1}. The intensity of the absorption band in the range 1000 – 1150 cm^{-1} increases with increasing B_2O_3 content.

The synthesis of mixtures containing 20 – 30% La_2O_3, 40 – 50% SiO_2, and 30 – 60% B_2O_3 (compositions 2, 5, 8, 12) yields a stable glassy state.

The refractive index of glass samples showing no indications of phase separation is 1.63 – 1.72. The CLTE of the experimental glasses varies in the range (60 – 70) × 10^{-7} K^{-1} and increases with increasing lanthanum oxide content.

An assessment of the heat treatment of the samples in the temperature range 600 – 1050°C in a gradient electric furnace revealed showed regular behavior: samples with 20% La_2O_3 are characterized by the presence of a crystalline film while increasing the content of La_2O_3 to 30% intensifies crystallizability right up to volume crystallization.

The viscosity of the experimental glasses in the range 10^{10} – 10^4 Pa · sec was measured with a PPV-1000 viscosimeter (Orton Company, USA) by compressing a 10 mm in diameter, 6 mm high cylindrical sample.

Increasing the lanthanum oxide content from 20 to 30% (compositions 2 and 5) as the expense of SiO_2 has a large effect on the temperature dependence of the viscosity, increasing it in the range 10^{10} – 10^6 Pa · sec and lowering the high-temperature viscosity (Fig. 3). Therefore it can be concluded that the solidification rate of glass increases with increasing content of this component.

As less and less SiO_2 is introduced instead of B_2O_3, the viscosity decreases by 1.5 – 2 orders of magnitude at 30% La_2O_3.

As the lanthanum oxide increases from 20 to 30%, the B_2O_3 content introduced instead SiO_2 remaining constant, the [BO_3] fraction in the IR spectra of the experimental glasses increases. The degree of polymerization of the silicon-oxygen tetrahedra decreases, as is indicated by the van-

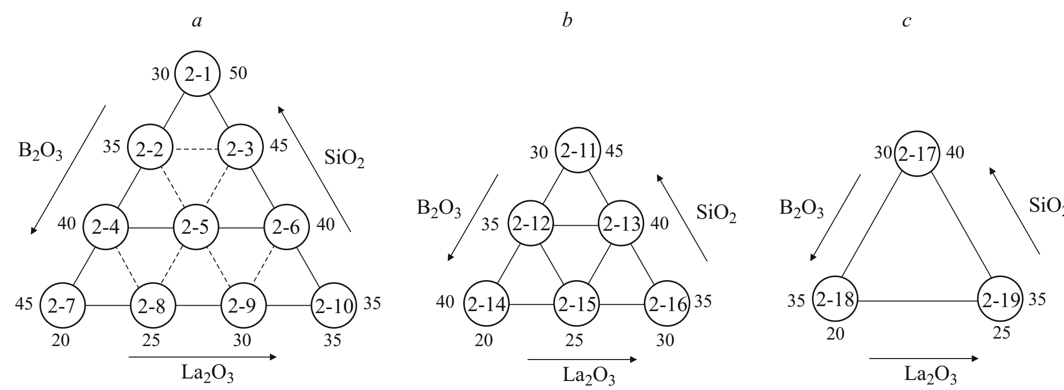

Fig. 4. Compositions of La_2O_3–B_2O_3–TiO_2–SiO_2 glass: *a*) no TiO_2; *b*) 5% TiO_2; *c*) 10% TiO_2.

ishing of the peak at 1080 cm^{-1} of the main absorption band in the range 900 – 1100 cm^{-1}.

In summary, the glass compositions distinguished by the stability of the glassy state were determined from a study of the system La_2O_3–B_2O_3–SiO_2. The following composition ranges were singled out for a more detailed study of the glasses, %: 20 – 35 La_2O_3, 25 – 50 SiO_2, and 30 – 45 B_2O_3. The compositions and qualitative characteristics of the glasses are presented in Fig. 4.

Glass containing 35 – 45% B_2O_3 and 20 – 25% La_2O_3 is prone to liquation phase separation. It must be assumed that a stable liquation dome, which manifests above the liquidus, is present in the experimental region of the system La_2O_3–B_2O_3–SiO_2. The continuation of the stable liquation dome into the region below the liquidus gives rise to metastable liquation separation, which is why the samples containing 20 – 25% La_2O_3 are opacified. In addition, one of the liquating phases is prone to crystallization with $LaBO_3$ crystals precipitating.

Since La_2O_3–B_2O_3–SiO_2 glass does not have the required refractive index, glass with partial sections of the system La_2O_3–B_2O_3–TiO_2–SiO_2 with 5, 10, and 15% TiO_2 were synthesized at the next stage of this work.

Titanium oxide lowers the glassmaking temperature — glass synthesizes at 1350°C — and suppresses stable liquation processes. The glass samples were characterized by uniformity and transparency.

The physical-chemical properties of La_2O_3–B_2O_3–TiO_2–SiO_2 glass are presented in Table 1.

TiO_2 increases the refractive index of glass to 1.70 – 1.73, increases the average dispersion, and correspondingly decreases the dispersion coefficient to 41. The CLTE of the experimental glass increases with increasing La_2O_3 content because the covalence of the bonds decreases.

Gradient heat-treatment of La_2O_3–B_2O_3–TiO_2–SiO_2 glass at temperatures 600 – 1050°C for 6 h showed that the lanthanum oxide content strongly affects crystallizability. For example, glass samples with 20% La_2O_3 are prone to surface crystallization, which is manifested as the formation of a surface film. Samples with 25 – 30% La_2O_3 are even more prone toward crystallization. Volume crystallization is characteristic for samples containing 10 – 15% TiO_2, for which the volume crystallization interval widens as SiO_2 content decreases.

The character of the crystallization of heat-treated samples also depends on their TiO_2 content. For 15% TiO_2 a fine crystalline phase consisting mostly of rutile is present.

Studies of La_2O_3–B_2O_3–TiO_2–SiO_2 glass show that TiO_2 can eliminate the stable liquation that is characteristic for lanthanum-borosilicate glass. The refractive index of titanium-containing glass increases to 1.735. However, the proneness of titanium-containing glass toward crystallization is quite high, which is manifested in volume crystallization of such glass with 6-h heat treatment in a gradient electric furnace. When more than 10% TiO_2 is introduced into La_2O_3–B_2O_3–SiO_2, glass rutile precipitates during heat treatment. The compositions 11, 12, and 14 with 20% La_2O_3 and 10% TiO_2 were chosen to optimize the composition of high refractive-index glass.

To decrease crystallizability the La_2O_3–B_2O_3–TiO_2–SiO_2 glass compositions were made more complicated by introducing barium oxide in amounts up to 30% keeping the La_2O_3 and TiO_2 contents constant at 20 and 10%, respectively. The glass compositions are presented in Fig. 5.

TABLE 1. Physical-Chemical Properties of La_2O_3–B_2O_3–TiO_2–SiO_2 Glass

Composition No.*	Refractive index	Average dispersion	Dispersion coefficient	CLTE, 10^{-7} K^{-1}	Density, kg/m^3
2-11	1.6692	0.01314	50.9	53.2	3960
2-12	1.6760	0.01317	51.3	54.8	3970
2-13	1.6995	0.01406	49.8	55.9	4310
2-14	1.6828	0.01320	51.7	54.0	3980
2-15	1.7062	0.01409	50.1	60.2	4320
2-16	1.7298	0.01497	48.7	67.0	4650
2-17	1.7020	0.01553	45.2	55.4	4030
2-18	1.7087	0.01556	45.6	56.1	4040
2-19	1.7322	0.01644	44.5	62.4	4390
2-20	1.7347	0.01791	41.0	58.5	4110

* TiO_2 content: 5% (glasses 2-11 – 2-16); 10% (2-17 – 2-19); 15% (2-20).

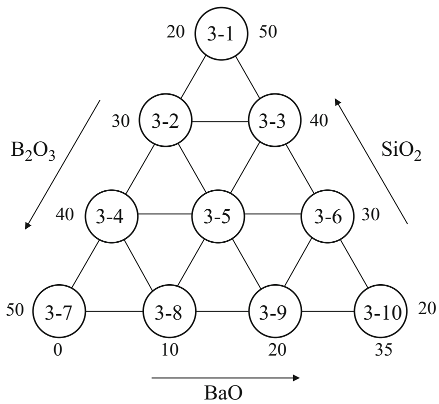

Fig. 5. $BaO–La_2O_3–B_2O_3–TiO_2–SiO_2$ glass compositions with constant contents 20% La_2O_3 and 10% TiO_2.

TABLE 2. Physical-Chemical Properties of $BaO–La_2O_3–B_2O_3–TiO_2–SiO_2$ Glass

Composition No.	Refractive index	Average dispersion	Dispersion coefficient	CLTE, $10^{-7}\ K^{-1}$	Density, kg/m^3
3-1	1.6885	0.0155	44.5	62.5	4010
3-2	1.7020	0.0155	45.2	61.7	4030
3-3	1.7435	0.0170	43.6	70.5	4410
3-4	1.7155	0.0156	48.9	60.4	4050
3-5	1.7570	0.0171	44.2	69.3	4420
3-6	1.7985	0.0186	42.8	79.1	4810
3-7	1.7290	0.0156	46.6	59.6	4070
3-8	1.7705	0.0172	44.9	67.5	4450
3-9	1.8120	0.0187	43.4	76.8	4830
3-10	1.8535	0.0202	42.2	86.4	5240

It should be noted that because barium-containing glass melts are highly corrosive synthesis was conducted in platinum crucibles at temperature 1250 – 1300°C.

The optical and thermal properties of $BaO–La_2O_3–B_2O_3–TiO_2–SiO_2$ glass are presented in Table 2.

The refractive index of the experimental glasses varies from 1.68 to 1.85 and increases in a regular manner with increasing BaO content. Likewise, the CLTE of the glasses in the experimental composition range is determined mainly by the barium oxide content and lies in the range $(59 – 86) \times 10^{-7}\ K^{-1}$.

Studies of the crystallizability of the experimental glasses of the system $BaO–La_2O_3–B_2O_3–TiO_2–SiO_2$ have established that barium oxide can increase the stability of the glassy state.

In contrast to glasses of the base system $La_2O_3–B_2O_3–TiO_2–SiO_2$ with 20 – 60% La_2O_3, which are characterized by volume crystallization during heat treatment, $BaO–La_2O_3–B_2O_3–TiO_2–SiO_2$ glass with 20% La_2O_3 tend to undergo surface crystallization.

High refractive-index (1.75 – 1.79) $BaO–La_2O_3–B_2O_3–TiO_2–SiO_2$ glasses was chosen on the basis of their technological properties, specifically, their crystallizability. These glasses contain 30% SiO_2, 20 – 30% B_2O_3, and 10 – 20% BaO.

The composition of high refractive-index glass was optimized by varying the components of the system $BaO–La_2O_3–B_2O_3–TiO_2–SiO_2$ with step 2% as well as by adding ZrO_2 and Nb_2O_5 in amounts from 2 to 6%. This yielded glass with refractive index 1.81, average dispersion 0.0187, and CLTE $76.8 \times 10^{-7}\ K^{-1}$. This glass can be recommended for obtaining highly refractive optical lenses. An important application of optical glass with refractive index about 1.8 is for the light-guiding core of optical fibers. A numerical aperture of the optical fiber equal to 1.03 is obtained with VO-50 and VTO-73 light-reflecting, protective cladding.

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